MIDTERM #2 - SOLUTIONS

CHM 2120 3X

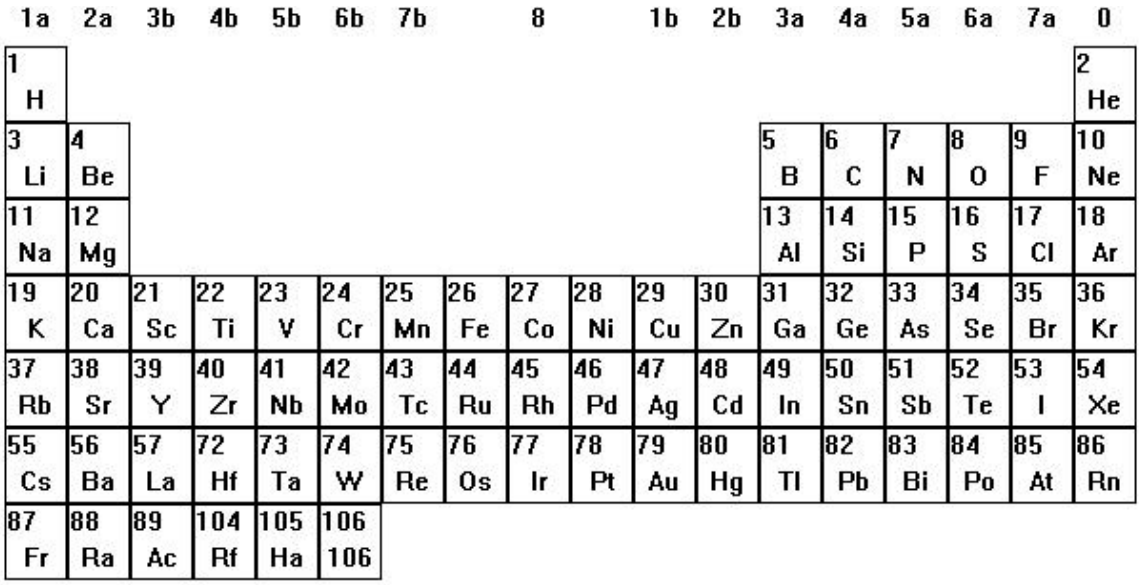
Prof: Mark Dornan

Last name: _____ **First name:**_____

Student #:_____ **Date:** July 14th 2015

Notes:

- Approximate total number of points: 64
- There are 9 pages in this exam
- Molecular models are allowed
- Re-grade requests for exams written in pencil will not be considered

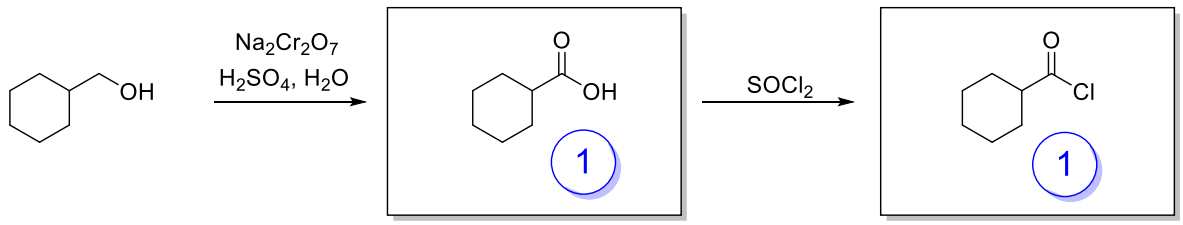


pK_a table

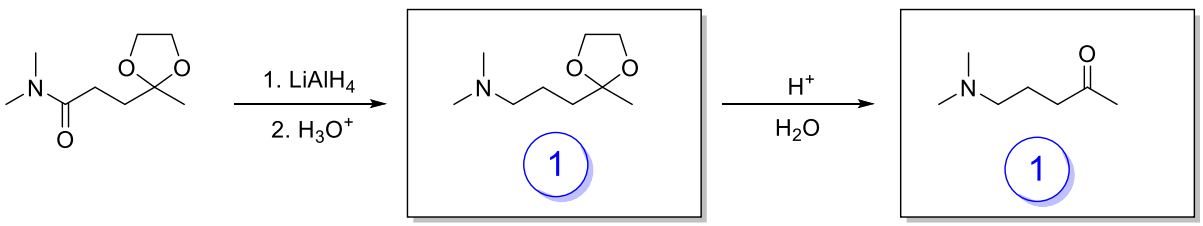
Acid	pK_a
HBr	-9
ROH_2^+	-2
H_3O^+	-1.75
RCO_2H	5
R_3NH^+	10-11
H_2O	15.75
ROH	16-18
$RC(O)CH_3$	20
$HC{\equiv}CH$	25
H_2	36
R_2NH	35-40
$CH_2{=}CH_2$	44
RCH_3	55

1. Fill in the missing structures or reagents (**10 marks**).

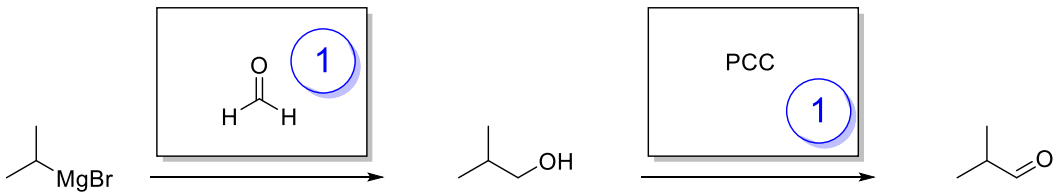
a.



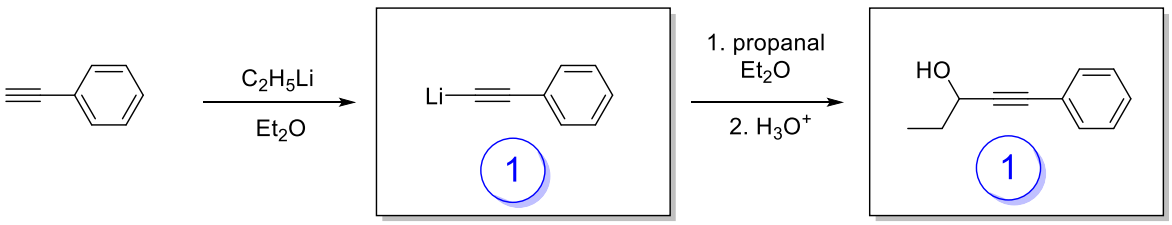
b.



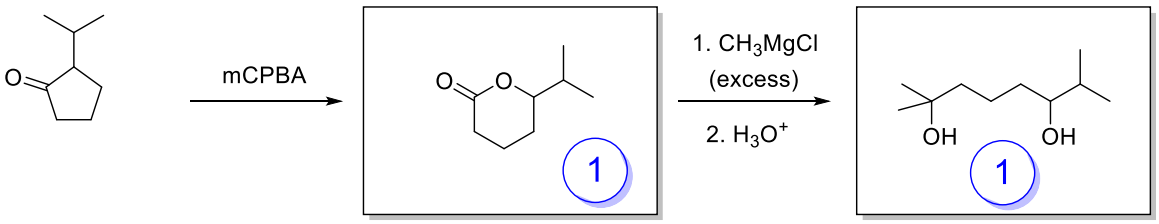
c.



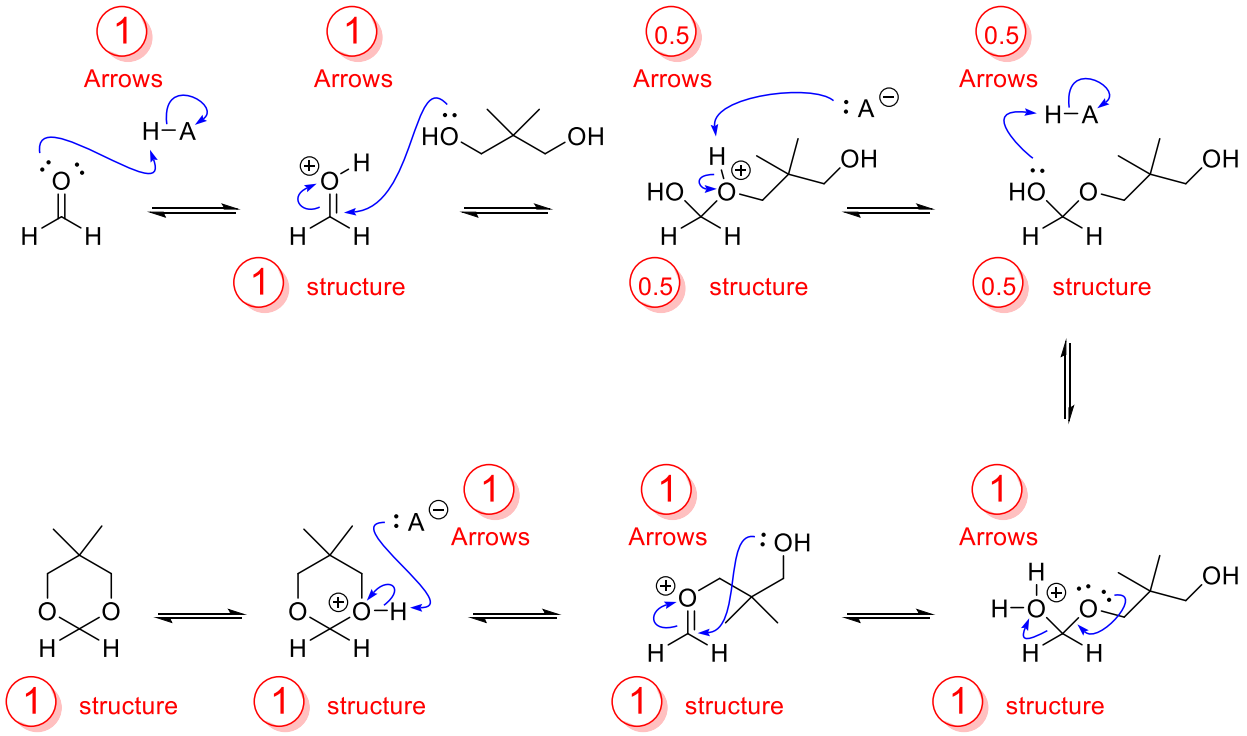
d.



e.

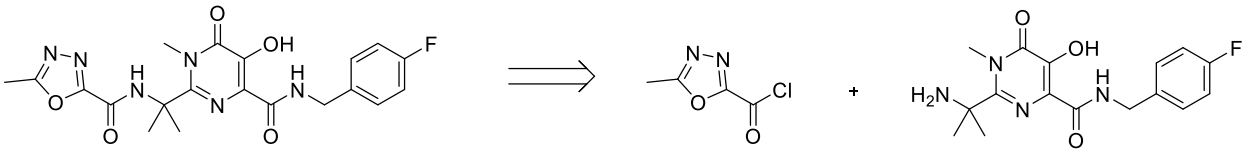


2. Provide a detailed mechanism for the formation of the major product of the reaction of 2,2-dimethyl-1,3-propanediol with acetone in the presence of an acid catalyst. (**12 marks**)



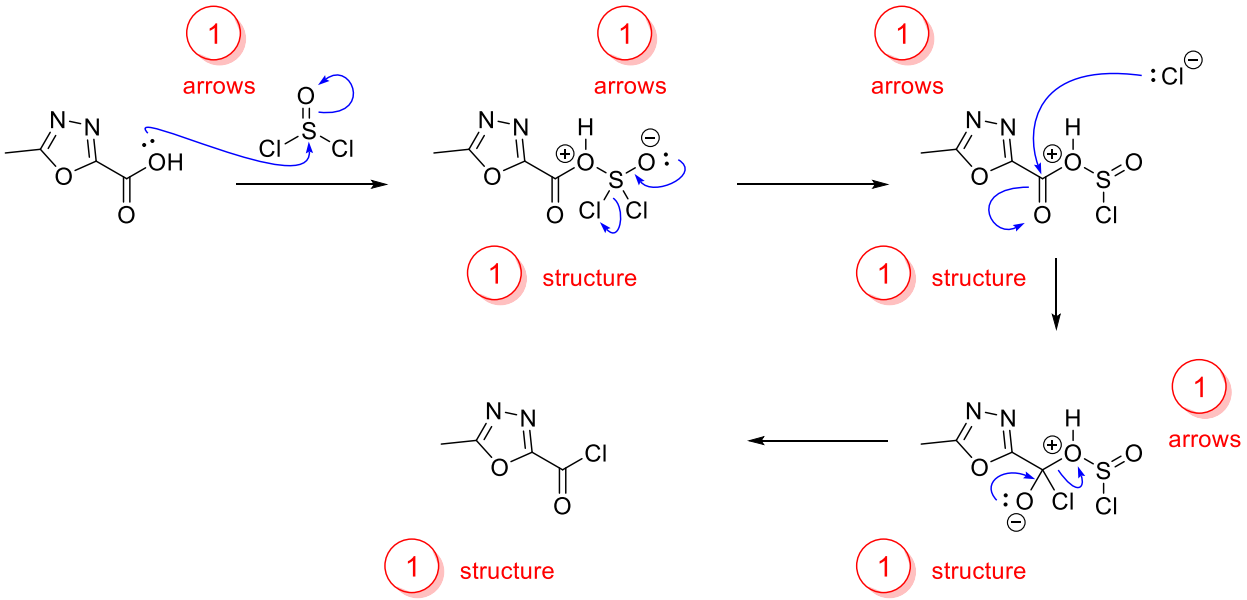
Doesn't matter which acid catalyst is used.
Doesn't matter what they use to do the proton shuttle (A- or another molecule of the diol)

3. Raltegravir is an HIV-integrase inhibitor developed by Merck which is used to treat HIV infection in children. The last step of the synthesis involves an amide bond forming reaction between the two starting materials shown below.

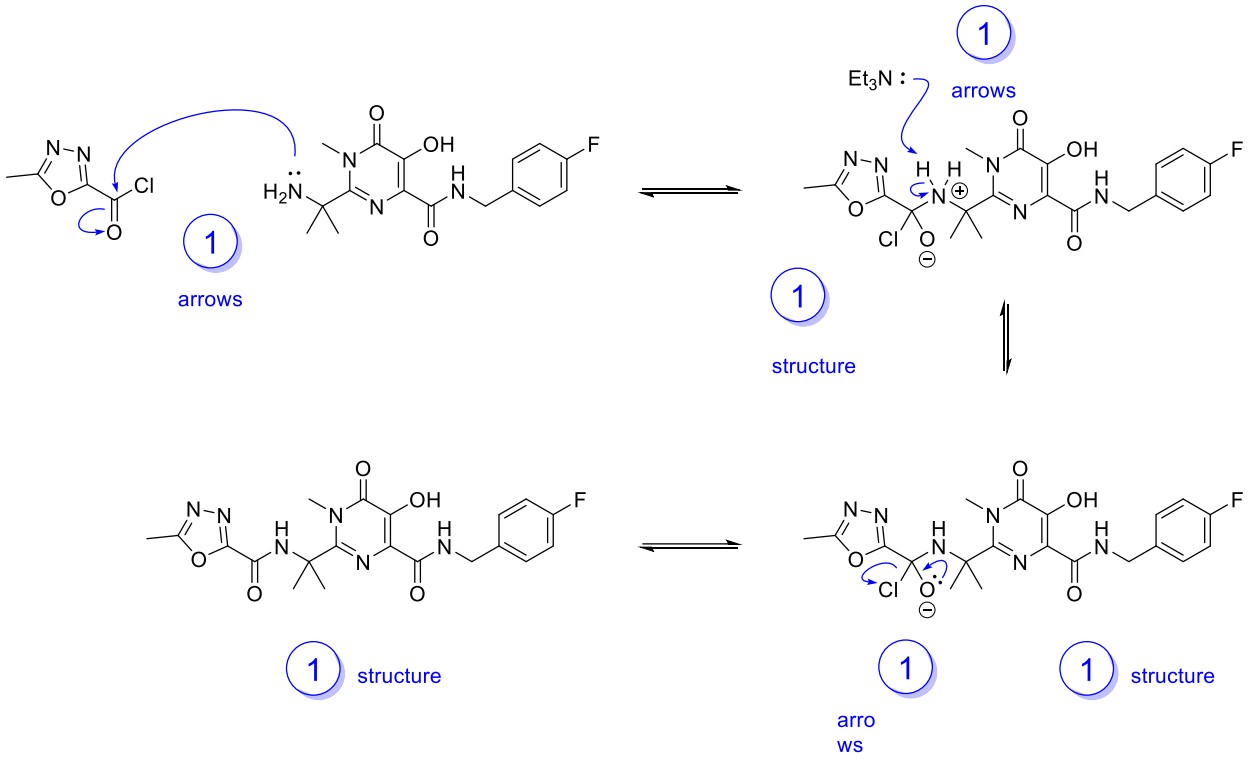


Raltegravir **Fragment A** **Fragment B**

a. Draw a detailed mechanism for the formation of Fragment A from the corresponding carboxylic acid using any additional reagents necessary (**8 marks**).

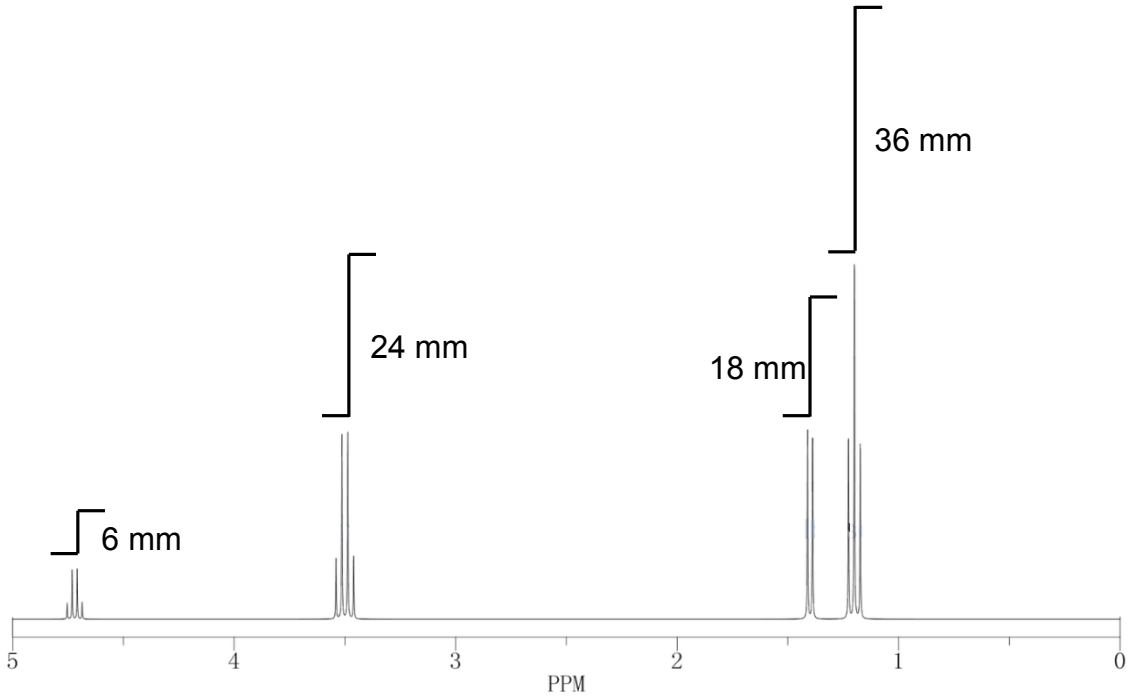


b. Draw a detailed mechanism of the formation of Raltegravir using Fragment A, Fragment B and any additional reagents necessary. (**6 marks**)



Any base acceptable. Can also use another equiv of amine as base

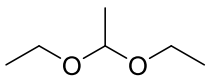
4. An unknown compound has the formula $C_6H_{14}O_2$. Fill in the table (**5 marks**) and elucidate the structure of the molecule by analyzing the following ^1H NMR spectrum. (**5 marks**)



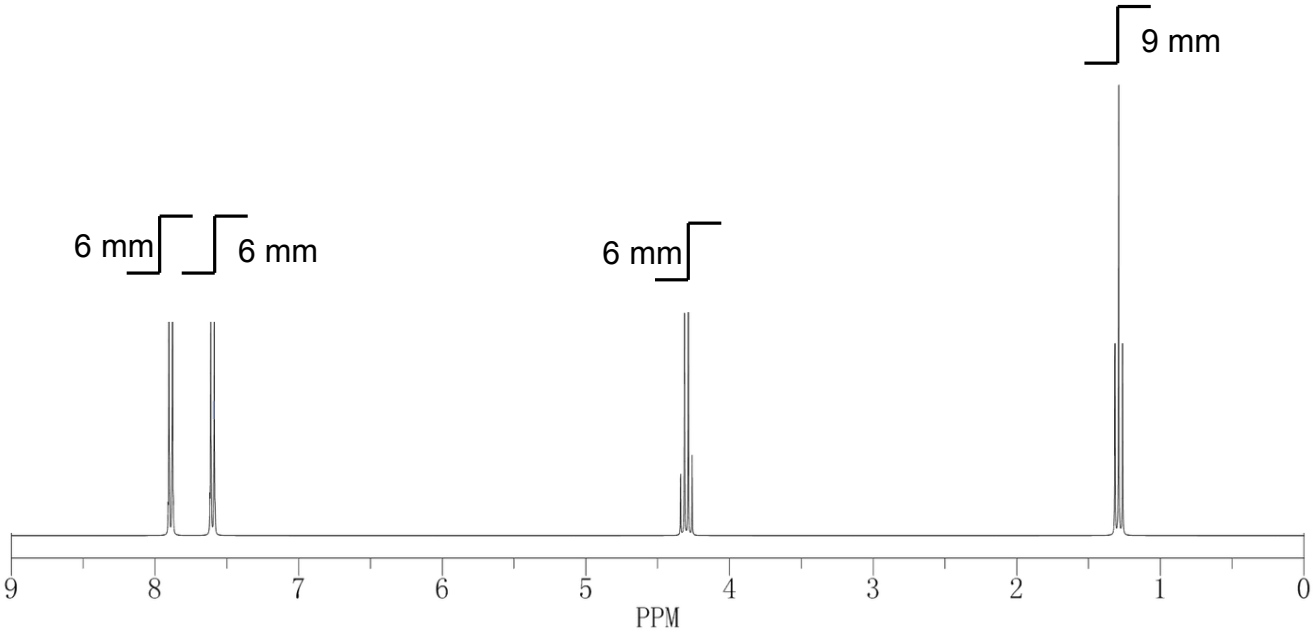
Signal	δ	Integration	Multiplicity	Ideas
A	4.7	1H	q, n=3	O-C**H**–CH3
B	3.5	4H	q, n=3	O-C**H2**-CH3
C	1.4	3H	d, n=1	C**H3**-CH
D	1.2	6H	t, n=2	**CH3**-CH2

1 mark for filling in chemical shift column correctly, 1 mark for filling in integration column correctly, 1 mark for filling in multiplicity column correctly, plus up to 2 marks for any correct ideas. If answer is wrong, up to 2 points for close ideas, or putting fragments together correctly.

Correct structure:



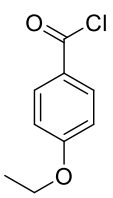
5. An unknown compound has the formula $C_9H_9O_2Cl$. An IR spectrum of the compound shows a sharp peak at 1750 cm^{-1}. Fill in the table (**5 marks**) and elucidate the structure of the molecule by analyzing the following ^1H NMR spectrum. (**5 marks**)



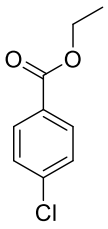
Signal	δ	Integration	Multiplicity	Ideas
A	7.9	2H	d, n = 1	Aromatic, symmetry, 2x Ar-H
B	7.6	2H	d, n = 1	Aromatic, symmetry, 2x Ar-H
C	4.3	2H	q, n = 3	**CH2**-CH3 connected to electroneg atom
D	1.3	3H	t, n = 2	CH2-**CH3**

1 mark for filling in chemical shift column correctly, 1 mark for filling in integration column correctly, 1 mark for filling in multiplicity column correctly, plus up to 2 marks for any correct ideas. If answer is wrong, up to 2 points for close ideas, or putting fragments together correctly.

Correct answer

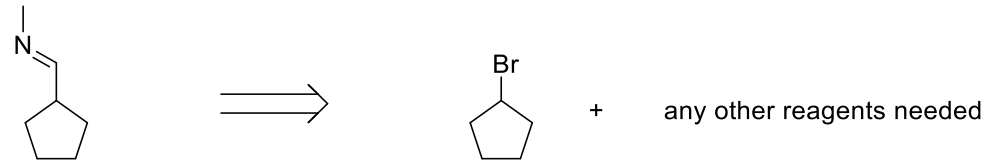


Also accepted for full marks:

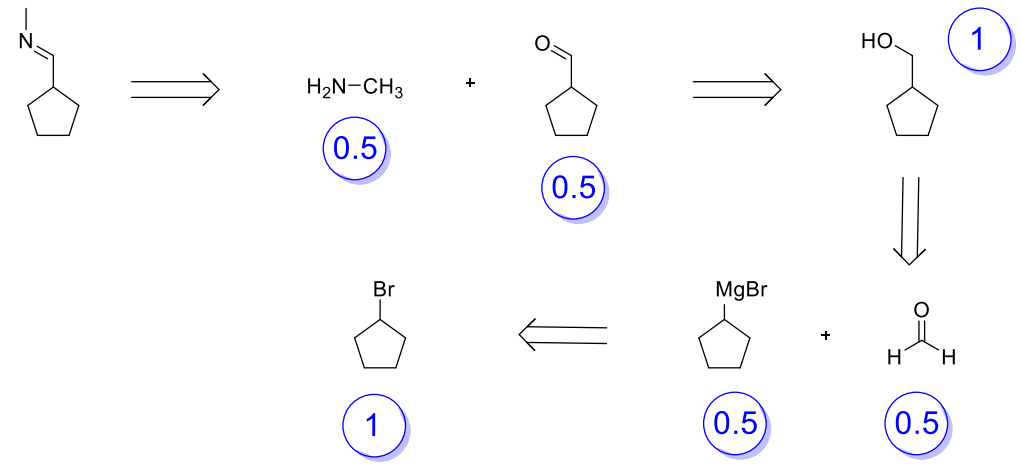


5

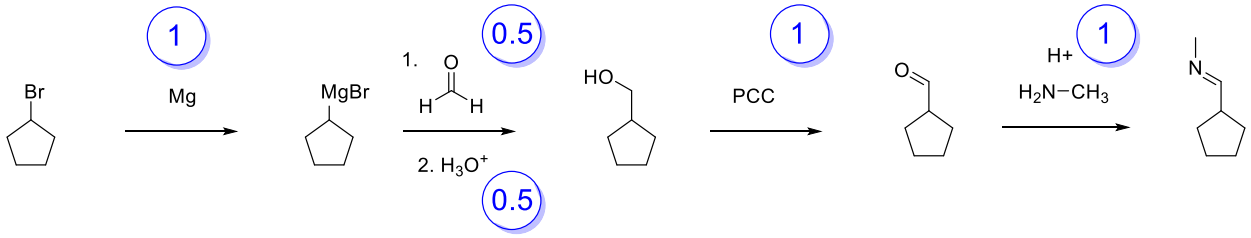
6. Design a synthesis of N-(cyclopentylmethylidene)-methanamine from bromocyclopentane. Include a retrosynthesis (**4 marks**), and the forward synthesis (**4 marks**) including any other reagents needed. Mechanisms are not required.



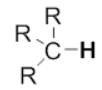
Retro



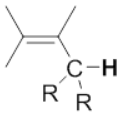
Synthesis



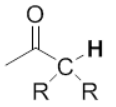
Typical ^{1}H chemical shifts



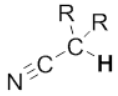
0.7 - 1.7



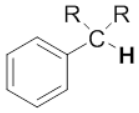
1.6 - 2.6



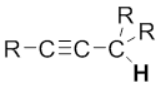
2.1 - 2.5



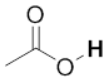
2.1 - 3.0



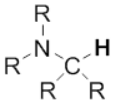
2.3 - 2.7



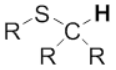
1.7 - 2.7



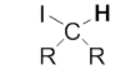
11.0 - 12.0



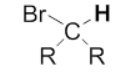
2.2 - 2.9



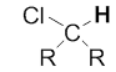
2.0 - 3.0



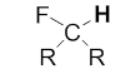
2.0 - 4.0



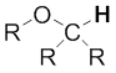
2.7 - 4.1



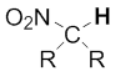
3.1 - 4.1



4.2 - 4.8

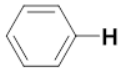


3.0 - 5.0



4.1 - 4.3

4.5 - 7.0



6.5 - 8.0

9.0 - 10.0

*** All are approximate**